

Low-Temperature-Fired ReVO_4 (Re = La, Ce) Microwave Dielectric Ceramics

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We report a series of ReVO_4 (Re = La, Ce) microwave dielectric ceramics fabricated by a standard solid-state reaction method. X-ray diffraction and scanning electron microscopy measurements were performed to explore the phase purity, sintering behavior, and microstructure. The analysis revealed that pure and dense monoclinic LaVO_4 ceramics with a monazite structure and tetragonal CeVO_4 ceramics with a zircon structure could be obtained in their respective sintering temperature range. Furthermore, LaVO_4 and CeVO_4 ceramics sintered at 850°C and 950°C for 4 h possessed out-bound microwave dielectric properties: $\epsilon_r = 14.2$, $Q \times f = 48197$ GHz, $\tau_f = -37.9$ ppm/°C, and $\epsilon_r = 12.3$, $Q \times f = 41\,460$ GHz, $\tau_f = -34.4$ ppm/°C, respectively. The overall results suggest that the ReVO_4 ceramics could be promising materials for low-temperature-cofired ceramic technology.

I. Introduction

WITH the emerging progress and revolutionary changes in the development of wireless communication technology over the past decades, the target of reducing the size and cost of filter, oscillator, and antenna components in applications ranging from cellular phones to global positioning systems has continuously stimulated the research of novel microwave dielectric materials.¹ Specifically, advanced substrate materials for microwave integrated circuits are earnestly required nowadays, and main characteristics with respect to this subject consist of a low permittivity (ϵ_r), a high quality factor ($Q \times f$), and a near-zero temperature coefficient of resonant frequency (τ_f) in a potential dielectric oxide ceramic. Another all-important factor that deserves high attention is associated with the low-temperature cofired ceramic (LTCC) technology, that is, the samples have to be sintered below the melting point of Ag (961°C) for being cofired with pure Ag electrode.

Up to now, a mass of promising low-loss dielectrics for advanced ceramic substrate materials have been extensively studied, including rare-earth orthoniobates ReNbO_4 (where Re is the rare-earth element), rare-earth orthophosphates RePO_4 , Zn_2SiO_4 , Mg_2SiO_4 , and MgAl_2O_4 ceramics.^{2–6} Unfortunately, they are counted out of the applications in LTCC-based devices on account of high sintering temperatures they suffer. A moderate amount of low-melting glasses and oxides additives were commonly introduced to improve this situation, whereas microwave dielectric properties were

deteriorated owing to the formation of some amorphous phases in the matrix.

The current research focus was thus placed on the discovery of new dielectric materials with intrinsically low sintering temperatures. Some Bi_2O_3 -, TeO_2 -, MoO_3 -, and B_2O_3 -based compounds have received extensive attention in this regard.^{7–11} Recently, it has been reported that V_2O_5 -rich low-firing ceramics could exhibit excellent microwave dielectric properties and good chemical compatibility with metal electrodes.^{12–14} The rare-earth orthovanadates ReVO_4 are a subset of the family of ABO_4 -type compounds and have been systematically investigated due to their various optical, magnetic, elastic, and electronic properties. The structure analysis under ambient conditions revealed that only LaVO_4 prefers to crystallize with a monoclinic monazite-type structure conforming to a space group $P2_1/n$ and other ReVO_4 compounds adopt a tetragonal zircon-type structure with $I4_1/amd$.¹⁵ In the monazite structure, $[\text{AO}_6]$ polyhedra are edge shared with $[\text{VO}_4]$ tetrahedra along the c axis, whereas the zircon structure consists of alternating $[\text{VO}_4]$ tetrahedra and edge-sharing $[\text{AO}_8]$ dodecahedra forming chains parallel to the c axis.^{16,17} To the best of our knowledge, their microwave dielectric properties have not been reported as yet. In this work, as representatives of the above-mentioned two kinds of crystal structures, LaVO_4 and CeVO_4 were synthesized by a conventional solid-state ceramic route. Their phase purity, sintering behavior, and especially microwave dielectric properties were studied for the first time.

II. Experimental Procedure

The ReVO_4 (Re = La, Ce) ceramics were synthesized by a conventional solid-state reaction route using high-purity powders of La_2O_3 , CeO_2 , and V_2O_5 . Stoichiometric amounts of chemical powders were weighed and ball-milled in distilled water for 4 h using zirconia balls. The resulting slurry was then rapidly dried and calcined at 600°C and 800°C for 4 h to obtain LaVO_4 and CeVO_4 powders, respectively. The calcined powders were remilled for 6 h and then mixed together with 5 wt% PVA as a binder. The granulated powders were subsequently pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. The specimens were first heated at 550°C in air for 4 h to remove the organic binder and then sintered at 775°C–900°C (for LaVO_4) and 875°C–1000°C (for CeVO_4) for 4 h, respectively.

The bulk densities of the sintered pellets were evaluated with the Archimedes method. The crystal structures of the fired ceramics were identified via an X-ray diffractometer (XRD; D/Max2500 V, Rigaku, Tokyo, Japan) using CuK_α radiation. The calculation of lattice parameters was accomplished using GSAS-EXPGUI program with the Rietveld refinement to fit the diffraction patterns. The refinement involved the lattice parameters, background, atomic coordinates, site occupancies, and isotropic thermal parameters as well as profile parameters (peak height and peak shape).¹⁸

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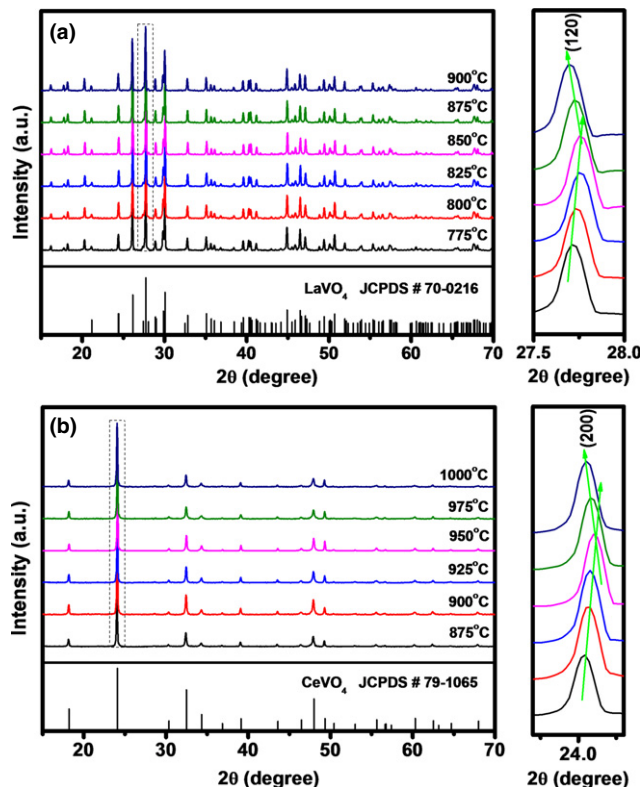


Fig. 1. XRD patterns of (a) LaVO_4 ceramics sintered at 775°C–900°C for 4 h and (b) CeVO_4 ceramics sintered at 875°C–1000°C for 4 h.

The microstructure of the pellets was observed by a scanning electron microscope (SEM; JSM-6490LV, JEOL, Tokyo, Japan). Microwave dielectric properties of the sintered ceramics were measured using a network analyzer (N5230C; Agilent, Palo Alto, CA) and a temperature chamber (GDW-100; Saiweisi, Changzhou, China). The τ_f values of the samples were measured in the temperature range from 20°C to 80°C and calculated by the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2 , respectively.

III. Results and Discussion

Figures 1(a) and (b) depict the XRD patterns of the ReVO_4 ceramics sintered in their respective temperature range. Observably, the reflection peaks of LaVO_4 matched well with those of a monoclinic monazite structure (JCPDS #70-0216). On the other hand, CeVO_4 was confirmed to a tetragonal zircon structure (JCPDS #79-1065). It was reported that the monoclinic phase of CeVO_4 could develop as it was synthesized at temperatures lower than 400°C, whereas a tetragonal one could be stabilized at higher synthesis temperatures.¹⁹ Of particular note is that the main peaks (120) of LaVO_4 and (200) of CeVO_4 firstly shifted toward higher angles and then toward lower angles with increasing firing temperatures. Herein, Rietveld refinement was employed to illustrate such anomaly in the two ceramics. The refinement results of ReVO_4 samples sintered at 850°C (for LaVO_4) and 950°C (for CeVO_4) for 4 h are presented in Fig. 2. The refined unit cell volume and reliable factors are listed in Table I. As can be clearly seen from Table I, the unit cell volumes of ReVO_4 compounds first declined monotonously,

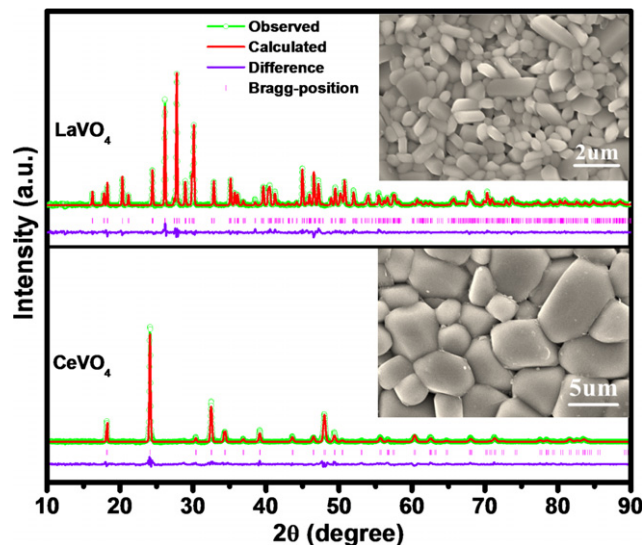


Fig. 2. Rietveld refinement patterns of LaVO_4 and CeVO_4 ceramics sintered at 850°C and 950°C for 4 h, respectively. Insets are the corresponding SEM images of the above two ReVO_4 ceramics.

Table I. Refined Unit Cell Volume, Reliability Factors, and Goodness-of-Fit Indicator of ReVO_4 Ceramics

Compounds	S.T (°C)	Unit cell volume (Å^3)	R_{wp} (%)	R_p (%)	χ^2
LaVO_4	775	331.78	7.59	5.87	0.585
	800	331.70	7.48	5.48	0.426
	825	331.56	4.99	3.58	0.513
	850	331.40	7.64	5.84	0.340
	875	331.53	5.76	4.15	0.690
	900	331.66	6.41	4.87	0.618
CeVO_4	875	353.44	7.81	6.20	1.951
	900	353.43	8.15	5.94	1.639
	925	353.40	7.49	5.46	1.557
	950	353.38	6.76	5.38	1.131
	975	353.42	7.37	5.52	1.402
	1000	353.52	8.83	6.28	2.005

R_{wp} , the reliability factor of weighted patterns; R_p , the reliability factor of patterns; χ^2 , goodness-of-fit indicator = $(R_{wp}/R_{exp})^2$.

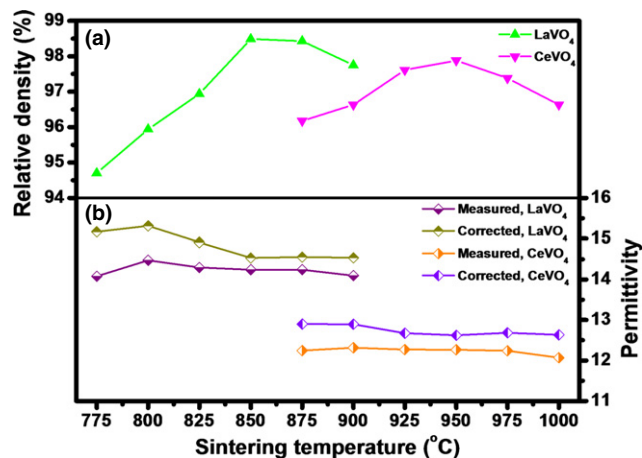


Fig. 3. The variation in (a) relative density and (b) permittivity of ReVO_4 ceramics sintered in their respective temperature range.

and then increased after reaching their respective minimum values with the increment of sintering temperature. The possible evaporation of vanadium might account for this kind of reduction in unit cell volumes because similar

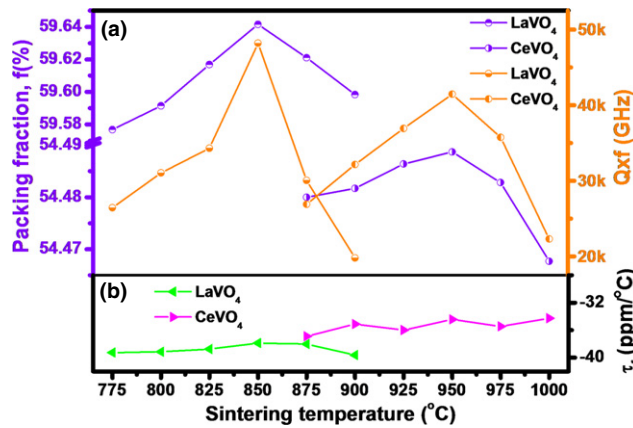


Fig. 4. The variation in (a) $Q \times f$ and packing fraction, and (b) τ_f of ReVO_4 ceramics sintered at different temperatures.

phenomenon has also been found in $\text{Ca}_5\text{Co}_4(\text{VO}_4)_6$ ceramics.²⁰ Moreover, a slight lattice expansion at higher sintering temperatures was probably due to the valence alternation of V atoms, as the existence of V^{4+} with larger ionic radius than V^{5+} will lead to the increment of the unit cell volumes.²⁰ The insets of Fig. 2 present the SEM micrographs of ReVO_4 samples sintered at 850°C (for LaVO_4) and 950°C (for CeVO_4) for 4 h. As representative samples, it can be seen that these two ceramics exhibited a homogeneous microstructure and evidently identifiable grain boundaries. The grains were compactly packed and the possible evaporation of vanadium might be responsible for the existence of few pores in the matrix. The same phenomenon has happened in $\text{Li}_2\text{ATi}_3\text{O}_8$ (A = Mg, Zn) ceramics.²¹

Figure 3(a) illustrates the variation in relative density of ReVO_4 ceramics sintered at various sintering temperatures for 4 h. All samples possess good densification behavior because the relative densities of most compounds are higher than 95%. After the maximum values were obtained at 850°C (for LaVO_4) and 950°C (for CeVO_4), a slight decrement of relative densities with increasing firing temperatures was considered to be a result of both the evaporation of vanadium and the abnormal grain growth at relatively high temperatures. As plotted in Fig. 3(b), the measured permittivity values (ϵ_{meas}) first increased and then dropped steadily with increasing sintering temperature. The porosity corrected values (ϵ_{corr}) were generally higher than the measured ones and they behaved in a similar tendency, as calculated by the following equation:²²

$$\epsilon_{\text{meas}} = \epsilon_{\text{corr}} \left(1 - \frac{3P(\epsilon_{\text{corr}} - 1)}{2\epsilon_{\text{corr}} + 1} \right) \quad (2)$$

where P is the porosity fraction.

The $Q \times f$ values of ReVO_4 ceramics sintered at different temperatures for 4 h are demonstrated in Fig. 4(a). With increasing sintering temperature, the $Q \times f$ values continuously increased to a maximum value and thereafter decreased, exhibiting a similar tendency as the variation in density. The highest $Q \times f$ values of 48 197 GHz for LaVO_4 and 41 460 GHz for CeVO_4 were yielded at 850°C and 950°C, respectively. Generally, $Q \times f$ of a composition depends on intrinsic parameters such as structural characteristics and extrinsic parameters such as porosity, secondary phases, lattice defects, impurity, and microstructural characteristics.²³ As mentioned above, ReVO_4 samples possessed high densities of >95% and no secondary phases were detected. These extrinsic impacts on $Q \times f$ could be thus out of consideration. According to the study of Kim *et al.*,²⁴ the $Q \times f$ value also could be largely dependent on the packing fraction (f) defined by summing the volume of packed ions

(V_{PI}) over the volume of a primitive unit cell (V_{PUC}), as expressed by the following equation:

$$f(\%) = \frac{V_{\text{PI}}}{V_{\text{PUC}}} \times Z \quad (3)$$

where Z is the number of atoms per unit cell. The calculated packing fraction results are presented in Fig. 4(a), which keep a good consistency with the $Q \times f$ values as a function of sintering temperature. Therefore, the packing fraction could be employed to interpret the variation in $Q \times f$ values in ReVO_4 samples. Moreover, the τ_f values versus firing temperature curves are presented in Fig. 4(b). No remarkable change in τ_f values was found with increasing sintering temperature and they fluctuated around a constant value of approximately -39 ppm/°C for LaVO_4 and -35 ppm/°C for CeVO_4 , respectively.

IV. Conclusions

A series of ReVO_4 microwave dielectric ceramics with low-firing temperature were synthesized using a conventional solid-state method. Monoclinic LaVO_4 with a monazite structure and tetragonal CeVO_4 with a zircon structure were yielded in the whole sintering temperature range. The samples sintered at 850°C (for LaVO_4) and 950°C (for CeVO_4) for 4 h exhibited excellent microwave dielectric properties: $\epsilon_r = 14.2$ and 12.3, $Q \times f = 48\,197$ and 41 460 GHz, and $\tau_f = -37.9$ ppm/°C and -34.4 ppm/°C, respectively. The inherently low-firing temperatures as well as potential microwave dielectric properties indicate that ReVO_4 compounds might be suitable candidates for advanced substrate materials in LTCC applications.

Acknowledgments

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